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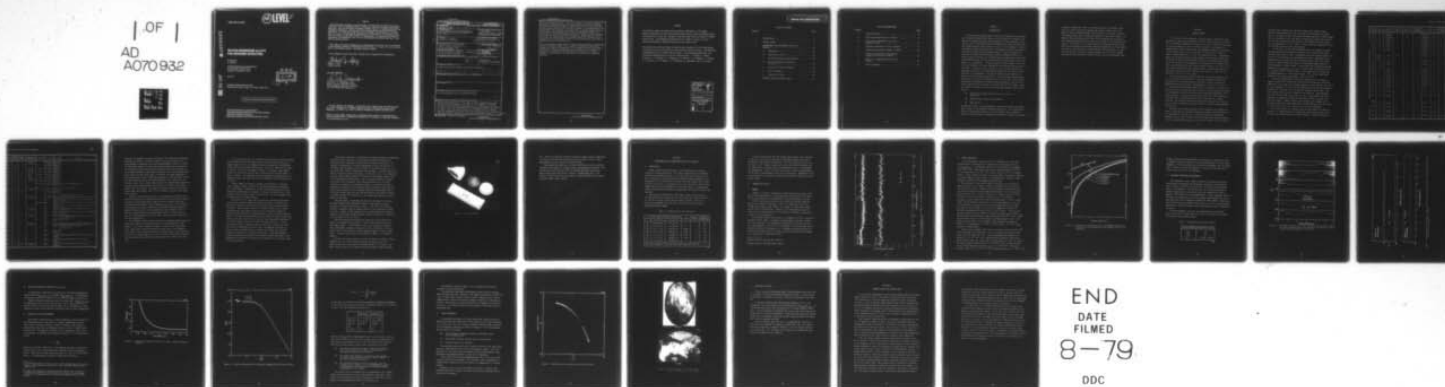
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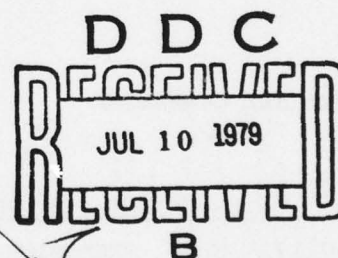
SILICON-GERMANIUM ALLOYS FOR INFRARED DETECTORS

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April 1979

TECHNICAL REPORT AFML-TR-79-4043
Interim Report for Period 15 August 1977 through 14 August 1978



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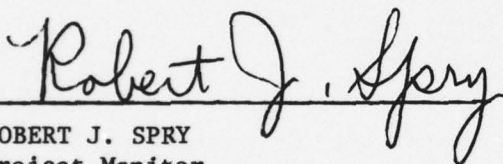
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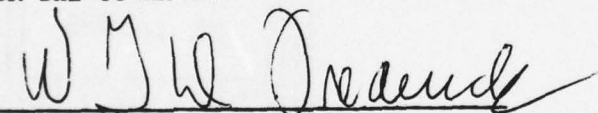
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FOR THE COMMANDER


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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER AFML TR-79-4043	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) SILICON-GERMANIUM ALLOYS FOR INFRARED DETECTORS.	5. TYPE OF REPORT & PERIOD COVERED Interim Report Aug 15 1977 - Aug 14 1978	
6. PERFORMING ORG. REPORT NUMBER		
7. AUTHOR(s) H./Winston H./Kimura	8. CONTRACT OR GRANT NUMBER(s) F33615-77-C-5052	
9. PERFORMING ORGANIZATION NAME AND ADDRESS Hughes Research Laboratories 3011 Malibu Canyon Road Malibu, CA 90265		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS Project No. 23060101
11. CONTROLLING OFFICE NAME AND ADDRESS Air Force Materials Laboratory (AFML/LPO) Air Force Systems Command Wright-Patterson AFB, OH 45433		12. REPORT DATE April 1979
13. NUMBER OF PAGES 33		14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) 12/36 p.
15. SECURITY CLASS. (of this report) UNCLASSIFIED		15a. DECLASSIFICATION DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) Interim rept. 15 Aug 77-15 Aug 78		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Silicon-germanium alloys, Czochralski growth		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Silicon-germanium alloys in the range of 10 at.% germanium have been prepared and investigated. The object of the program is to prepare intrinsic Si-Ge with high enough absorption at 1.06 μ m to be suitable for detectors at that wavelength and to investigate whether the changes in energy levels and optical properties of doped Si-Ge offer advantages for monolithic focal plane array applications over the corresponding doped silicon. The first year's work concentrated mostly on		

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growing intrinsic material. After some attempts to prepare crystals by growing a succession of seeds of increasing Ge content, we found that alloys with greater than 10% Ge could be grown by the Czochralski technique directly from 0.5% (or even 0%) Ge seeds if a suitable growth rate was chosen. The necessary slow growth rate to achieve single crystals necessitated long exposures of the melt to contamination from the crucible, but the use of high-purity synthetic quartz crucibles reduced the uptake of electrically active impurities. Measurements on alloys that were not intentionally doped yielded values for the shift in the energy level of boron from the case of a pure silicon host that were in agreement with the literature. 

Work now planned includes growth of purer material (either by refinements of the Czochralski method or by a pedestal technique), intentional doping with indium, investigation of the changes in device fabrication (oxidation, contacting, diffusion, etc.) required by the change from silicon to the alloy, and the fabrication of detectors to provide samples for evaluation of the potential of Si-Ge alloy as a detector material.

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PREFACE

This interim report describes work performed by personnel of the Hughes Research Laboratories, 3011 Malibu Canyon Road, Malibu, California 90265 during the period from 15 Aug 1977 through 14 Aug 1978 under Contract F33615-77-C-5052, Project 2306. The program was monitored by Dr. Robert J. Spry, Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio.

The program was directed toward the growth and evaluation of silicon-germanium crystals for use in P-i-N detectors and extrinsic detector arrays. The principal investigators were H. Winston and H. Kimura. The following people have also contributed significantly to the work reported here: C. Afable, P. Amini, R. Baron, J. P. Baukus, W. P. Fleming, M. F. Harvey, J. A. Henige, O. J. Marsh, K. T. Miller, D. J. O'Connor, A. F. Rabideau, R. Wong-Quen, and M. H. Young.

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TABLE OF CONTENTS

SECTION		PAGE
1	INTRODUCTION	1
2	CRYSTAL GROWTH	3
3	MEASUREMENTS AND EXPERIMENTS WITH Si-Ge CRYSTALS	11
	A. Composition	11
	B. Impurities in Si-Ge	12
	C. Spreading Resistance Measurements	16
	D. Optical Absorption Coefficient at 1.06 μm	19
	E. Analysis of Hall Measurements	19
	F. X-Ray Topographs	23
	G. Oxidation of Si-Ge	26
4	PRESENT STATUS AND FUTURE PLANS	27

LIST OF ILLUSTRATIONS

FIGURE		PAGE
1	Crystal C074 Ge	9
2	Electron microprobe scan of C064 Ge	13
3	Axial boron concentration of 1-in.- diameter crystal	15
4	Spreading resistance of Si-Ge crystals	17
5	Absorption spectrum of C077Ge at 296°K	20
6	Carrier concentration vs reciprocal temperature Si-Ge alloy C077Ge	21
7	Mobility vs temperature Si-Ge alloy C077Ge	24
8	X-ray topographs	25

SECTION 1

INTRODUCTION

The prospective applications of Si-Ge alloy materials to intrinsic and extrinsic photodetectors imply a list of goals for a research program on the preparation and characterization of these materials. One crucial issue is the possibility of preparing the alloys in highly perfect single-crystal form as ingots of 1-in. or 2-in. diameter. This is necessary because the silicon device technology we expect to extend to the alloy is based on large single crystals. Typical intrinsic Si detectors are fabricated from high-resistivity single-crystal 1-in. wafers, and the processes for infrared-sensitive monolithic focal plane arrays (MFPAs) begin with intentionally doped single-crystal wafers at least 2 in. in diameter. A second essential issue relates to the control and uniformity of alloy composition, both radially and axially, in the ingot. Since the virtue of using an alloy is the possibility of adjusting its optical and electronic properties by the choice of composition, it is important to be able to prepare alloy crystals of a definite and controllable composition. The third major requirement is that Si-Ge alloys must be prepared, just as in the case of Si, without significant contamination by unintentional impurities. Electrically active impurities must be kept at or below the 10^{12} cm^{-3} range. Thus, our work on the growth of Si-Ge alloys has been guided by the requirements of

- Crystallinity (good crystals up to 1 or 2 in. in diameter)
- Compositional control and uniformity
- High purity.

As discussed below, these requirements interact and careful attention must be paid to the tradeoffs inherent among them. Our original plan, based on information available in the literature, was to prepare a series of alloy crystals of gradually increasing Ge content, eventually

reaching a composition close to the desired 10% Ge value which could serve as a seed in the final growth. The low-Ge crystals were to be grown by the Czochralski method, and we expected to use some crucible-free growth method (such as pedestal growth) for the final crystal. We modified this plan when we found that 10% Ge crystals can be grown by the Czochralski method directly from 0.5% Ge seeds (or even from pure Si seeds). At present, we are concentrating on Czochralski growth as the most effective method of providing Si-Ge alloy material for characterization and for the fabrication of experimental photo-detectors. It may not be necessary to resort to pedestal growth at all in this program, although the decision awaits further results from the Czochralski work.

SECTION 2

CRYSTAL GROWTH

At the start of this program, we believed that a good Si-Ge alloy crystal of a particular composition could be grown only from a seed of not too different composition because of the strain caused by the change in lattice parameter as the Ge content increased. For example, it appeared that, with a 100% Si seed, the maximum allowable concentration in the crystal would be 3 at.% Ge. Such a crystal could in turn be used to provide seeds for a 5 at.% Ge crystal, and so on. Furthermore, growth of the alloy involves large changes in composition between melt and solid, as shown by the difference between the liquidus and solidus curves in the Si-Ge phase diagram. Such differences in composition can lead to interference with the crystal growth process in the form of constitutional supercooling and cellular growth. Earlier work indicated that growth rates below 10^{-4} cm/sec were necessary to avoid cellular growth at 10 at.% Ge in the crystal.

Since the growth rate usually employed in Czochralski growth of Si is on the order of inches/hour, we found it necessary to modify the mechanism of a Czochralski grower to provide a range of pull rates between 0.08 and 0.30 in./hr, corresponding to 6 to 20×10^{-5} cm/sec. It is apparent that prolonged growth runs are necessary to produce crystals even 1 in. long with such pull rates, and these long runs increase the contamination from the crucible and the internal atmosphere of the growth furnace. In an early run with Si alone to test the equipment, excessive oxide formation caused by small leaks into the chamber occurred. We found and repaired the leaks and installed a vacuum system to provide for growth in vacuum as well as in the helium atmosphere usually used.

The first Si-Ge crystals grown in this equipment were C056Ge and C057Ge. (The prefix C indicates Czochralski growth, and the symbol for Ge is appended to indicate that in these crystals the intentional "dopant" is Ge.) Both crystals were grown from melts having a composition of approximately $\text{Si}_{0.9}\text{Ge}_{0.1}$ at a rate of 2 mm/hr (6×10^{-5} cm/sec).

The runs were successful in that the crystals were largely single. However, their lengths were only 6 mm and 14 mm, which made it difficult to use them as seeds. Electron microprobe analysis of C057Ge showed that it contained 3.3 at.% Ge. Since the exact melt composition was 9.8 at.% Ge, the distribution coefficient of Ge between the solid and melt at this composition is 0.34. Table 1 lists the growth parameters for all the crystals grown so far in this program.

At this point, it had become apparent that the strategy of producing seeds with relatively small increments in Ge concentration would consume a great deal of time. Recognizing that this approach might still turn out to be necessary, we nevertheless decided to experiment with shortening the total process time by making larger steps in Ge concentration. Crystal C059Ge constituted an encouraging demonstration of the feasibility of larger steps. It was grown from a 300-g melt having composition $\text{Si}_{0.84}\text{Ge}_{0.16}$ at a rate of 2 mm/hr under less than 1 atm of He with the use of a [111] Si seed. The crystal was 15 mm long, had a maximum diameter of 2 mm, and was single. The crystal composition, measured by an electron microprobe, was 6.9 at.% Ge.

With this confirmation in hand, our next step was to attempt a larger crystal from a larger melt under otherwise identical conditions. C060Ge was 25 mm long, had a maximum diameter of 9 mm, and was 6.1 at.% Ge. Its only drawback as a source of seed material was that it was twinned, showing both [111] and [511] orientations along the growth axis. The next attempt, C061, was also twinned in the same way. The appearance of [511] - [111] twins is well known in Si. We speculated that [511] might be the preferred orientation and began a series of growth runs with [511] seeds. C062Ge, however, also twinned, not staying true to its seed orientation. Even though C061 and C062 twinned, they did result in crystals 24 to 25 mm in. long and up to 12 mm in diameter.

Up to this point, the crystals grown had been either too small or twinned. It seemed likely that twinning was associated with the transition from the original seed to a larger diameter. Again revising our

Table 1. Si-Ge Crystal Growth

Crystal Number	Melt Weight, g	Melt Composition	Growth Rate, mm/hr	Seed Rotation Rate, rpm	Crucible Rotation Rate, rpm	Ambient Gas	Orientation	Crystal Length, mm	Crystal Diameter, mm
C056	550	Si 0.902 Ge 0.098	2	10	4	He partial vacuum	<111>	6	4
C057	550	Si 0.899 Ge 0.101	2	10	8	He partial vacuum	<111>	14	3
C059	300	Si 0.84 Ge 0.16	2	8	8	He partial vacuum	<111>	15	2
C060	600	Si 0.84 Ge 0.16	2	8	8	He partial vacuum	<111>	25	9
C061	600	Si 0.84 Ge 0.16	2	8	8	He partial vacuum	<111>	24	12
C062	600	Si 0.84 Ge 0.16	2	8	8	He partial vacuum	<511>	25	12
C063						He partial vacuum	<511>	51	38
C064	Grown from C063	Si 0.66 Ge 0.34	0.5 to 1	10	13	He partial vacuum	<511>	25	25
C065	600	Si 0.64 Ge 0.36	1	10	13	He partial vacuum	<511>	13	13
C066	300	Si 0.98 Ge 0.02	13	10	13	He partial vacuum	<111>	89	27 to 29
C067	300								
C068	300	Si 0.72 Ge 0.28	1	10	13	He partial vacuum	<111>	8	25
C069	300	Si 0.96 Ge 0.04	5	10	18	He partial vacuum	<111>		
C070		Si 0.98 Ge 0.02	13	10	18	He partial vacuum	<111>		
C071	300	Si 0.72 Ge 0.28	0.5	10	18	He partial vacuum	<111>		
C072	300	Si 0.98 Ge 0.02	13	10	18	He partial vacuum	<111>		
C073	300	Si 0.72 Ge 0.28	0.5	10	18	He partial vacuum	<111>		
C074	300	Si 0.72 Ge 0.28	0.5	10	18	Vacuum	<111>	13	30
C075	307	Si 0.96 Ge 0.04	13	10	18	Vacuum	<111>		25
C077	304	Si 0.72 Ge 0.28	4	10	18	Vacuum	<111>	13	32
C079									
C082	295	Si 0.72 Ge 0.28	3	10	26	Vacuum	<111>		
C084	300	Si 0.72 Ge 0.28	0.5	10	26	Vacuum	<111>		
C085	300	Si 0.72 Ge 0.28	0.5	10	26	Vacuum	<111>		
C087	300	Si 0.72 Ge 0.28	0.5	10	26	Vacuum	<111>	18	45 max

1. Si-Ge Crystal Growth Summary

2

Orientation	Crystal Length, mm	Crystal Diameter, mm	Composition (Microprobe)	Crystallinity	Ge Source	Crucible	Remarks
<111>	6	4	Si 0.967 Ge 0.033	Single	Eagle Picher 69's	Regular Quartz	
<111>	14	3			Eagle Picher 69's	Regular Quartz	
<111>	15	2	Si 0.93 Ge 0.069		Eagle Picher 69's	Regular Quartz	
<111>	25	9	Si 0.94 Ge 0.061		Eagle Picher 69's	Regular Quartz	
<111>	24	12	Not analyzed		Eagle Picher 69's	Regular Quartz	
<511>	25	12	Not analyzed	Twinned	Eagle Picher 69's	Regular Quartz	
<511>	51	38	Ge 0.006	1/2 twinned	Eagle Picher 69's	Regular Quartz	
<511>	25	25		60% twinned	Eagle Picher 69's	Regular Quartz	Seed cut from longitudinal section.
<511>	13	13	Si 0.8643 Ge 0.1357	100% single	Eagle Picher 69's	Regular Quartz	Seed from CO64 crystal.
<111>	89	27 to 29			Eagle Picher 69's	Regular Quartz	
<111>	8	25	Si 0.9095 Ge 0.0905	100% single	Eagle Picher 69's	Regular Quartz	Run was aborted because of air leak.
<111>					Ortec	Regular Quartz	Seed - 1 in. shoulder { Growth terminated after 8 hours. Si 0.993, Ge 0.007
<111>					Ortec	Regular Quartz	Failed because scum formed on seed and prevented growth.
<111>					Ortec	Regular Quartz	1 in. diameter shoulder containing 1/2 at. % Ge used for seed.
<111>						Regular Quartz	1 in. diameter shoulder containing 1/2 at. % Ge used for seed.
<111>			Si 0.9938 Ge 0.0062		Ortec	Suprasil lined	12,000 Ω -cm on the skin, 4 point probe at ambient temperature.
<111>					Ortec	Suprasil lined	Run was aborted because bubbles formed in the Suprasil crucible.
<111>	13	30	Si 0.8923 Ge 0.1077		Ortec	Suprasil lined	Terminated. H ₂ O bubble formed in crucible lining. A slice was sent to Dr. Green, AFML.
<111>		25			Ortec	Suprasil lined	Seed crystal.
<111>	13	32	Si 0.8885 Ge 0.1115		Ortec	Suprasil heat-treated	Mostly single. Resistivity 2,000 - 6,000 Ω -cm, n-type. Resistivity 1700 Ω -cm after 650°C/1 hour anneal. Spreading resistance was measured.
<111>					Ortec	Suprasil heat-treated	Crucible cracked.
<111>					Ortec	Suprasil heat-treated	Approximately 200 Ω -cm (room temperature), p-type.
<111>					Ortec	Suprasil heat-treated	Run was aborted because crucible cracked.
<111>	18	45 max	Si 0.8836 Ge 0.1164		Ortec	Suprasil heat-treated	500 - 8000 Ω -cm (room temperature), p-type.

6397

strategy, we attempted to avoid carrying out the transition in material with high Ge content. Instead, we grew a 0.6 at.% Ge alloy out to a large diameter, intending to use this large-diameter crystal as a seed for subsequent growth of a 10% alloy. This procedure was also attractive because the high-concentration melt did not have to be exposed to the crucible during the long period of growth to the desired large diameter; growth from the large seed, or shoulder, can begin immediately after melting the charge. Using this approach, it was possible to grow the low-Ge shoulder out to the desired diameter at a rapid rate, say 13 mm/hr, since at the lower concentrations the constitutional supercooling and cellular growth difficulties do not set in until even higher growth rates are reached. The large shoulder was used as a seed with a high-Ge melt and a growth rate of 0.5 or 1 mm/hr to produce the high-Ge alloy crystal.

The first successful crystal by this procedure was C065Ge. Grown from a 36% Ge melt, its composition was 13.6% Ge and it was 100% single. The seed for this growth was a single section from C064, which had twinned during an attempt to grow high-Ge alloy from a low-Ge shoulder. This shoulder was part of C063, which had twinned halfway through its growth; C064 was grown by first melting back the twinned portion of C063 in a high-Ge melt and then growing it again. At this time, we were still experimenting with [511] seeds, and C063, C064, and C065 all had this orientation.

CP-4 etching of C064 clearly revealed the boundary between C064 and C063, which was also the growth interface at the beginning of C064 growth. It is convex toward the tang as a result of the slow growth rate. Many micro-cracks are observed on both sides of the boundary; the origin of these cracks could be the thermal shock of inserting C063 into the melt to grow C064, or it could be strain from lattice mismatch. The cracks terminate within the crystal and do not extend to the tang end.

Up to this point, most of our growth runs had been from 600-g charges and six-nines pure Ge from Eagle Picher and the crucibles had been of regular quartz. Since our emphasis had been primarily on establishing growth conditions for good crystallinity, we had not addressed the issues of purity. It was now worthwhile, however, to consider using higher-purity Ge, from Ortec, and the cost of this material dictated smaller melts of 300 g. The crucibles were also suspected of being sources of impurities that could limit the purity achievable even with high-quality Si and Ge.

Crystal C068 Ge was grown to assess the feasibility of growing from a charge as small as 300 g; our Czochralski grower was designed for a 1-kg charge. Although the crystal was misaligned with the rotational axis, which made it necessary to end the run after 8 hr, it was possible to grow a short length of 9% Ge alloy. In all subsequent runs, we used Ortec Ge and 300-g charges.

Other work in our laboratory had shown that synthetic high-purity silica wares available commercially under the names of Suprasil and Spectrosil, introduce less boron into Si melts than do regular quartz crucibles. These synthetic silica crucibles, however, have a lower softening point than regular quartz and are etched more rapidly by molten Si; both features are associated with a relatively high hydroxyl content. We expected that synthetic silica might not exhibit these drawbacks as seriously with Si-Ge as with Si, since the growth temperature of a 10% Ge alloy is about 70°C lower than that of pure Si. Crystal C072Ge was grown in a Suprasil-lined crucible from a dilute melt with the intent of producing a 0.67% Ge seed. The Suprasil was used as a liner so that the regular quartz crucible outer shell could provide mechanical stability at the growth temperature. Although alignment problems terminated the growth, the resulting crystal exhibited a room-temperature resistivity of 12000 Ω -cm, as measured by a four-point probe on the crystal skin.

This result caused us to reconsider the program strategy by suggesting that growth from a suitable crucible might provide high-resistivity material without requiring a crucible-free or pedestal technique. We decided to concentrate on crucible upgrading as the preferred route to obtaining high-resistivity Si-Ge suitable for intrinsic detectors. It was clear that crucible improvements were necessary. The next growth run, C073Ge, which was aimed at producing a 10% Ge alloy, had to be terminated because a large bubble formed on the bottom of the Suprasil-lined crucible and prevented further growth. The air trapped between the quartz outer shell and the Suprasil liner during fabrication of the lined crucible was suspected of causing the bubble. An attempt was made to alleviate the problem by evacuating the space between the liner and the shell during sealing, but the bubbling persisted during growth runs in the lined crucible made this way. The bubbling was unacceptable because it raised the level of the melt at a rate higher than the rate of withdrawal of the seed.

The persistence of bubbling even when care was taken to evacuate the space between shell and liner pointed to the presence of some precursor of a gas in the Suprasil itself. Since there is much more hydroxyl in Suprasil than in regular quartz, it was suspected of being the cause. Baking at high temperatures in vacuum reduced the hydroxyl content; the procedure finally adopted included a bake-out at 1300°C for 16 hr followed by 4 hr at 1420°C.

Before the bake-out procedure was available, crystal C074Ge was grown in a Suprasil-lined crucible. Its Ge content was 10.8%, and it was largely single. It was grown on one of the previously prepared low-Ge shoulders, reaching a diameter of 30 mm. Growth had to be terminated after 13 mm, however, because bubbles appeared in the crucible liner. A piece of this crystal was supplied to AFML. It is shown in Figure 1.

The most successful growth run so far was C077Ge, in which a 25-mm-diameter, 0.5% Ge, [111]-oriented shoulder was used as seed. The grown crystal was 13 mm long with a maximum diameter of 32 mm; it was mostly single except for a slightly misoriented grain toward the tang

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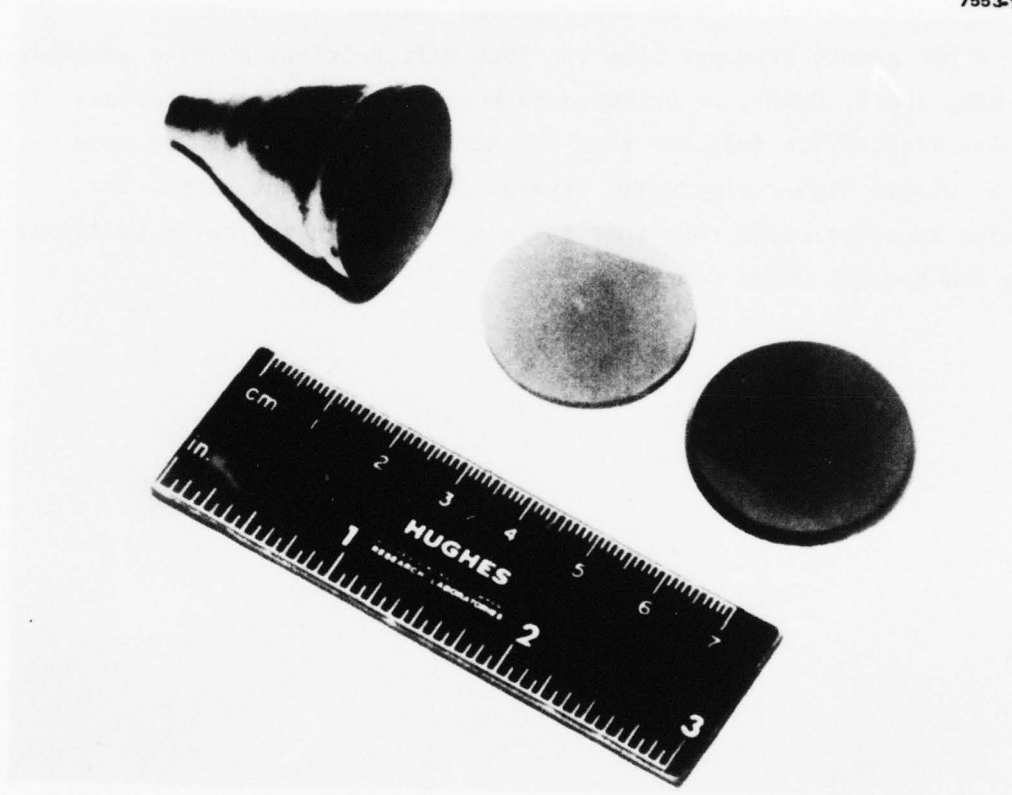


Figure 1. Crystal C074 Ge.

end. Electron microprobe analysis indicated a highly uniform composition of 11.2% Ge; the misoriented grain was also uniform at 11.4%. Other measurements on this crystal are reported below.

Other growth attempts have run into difficulties, such as crucible cracking (C079, C085), or produced rather low-resistivity material. The results with C077Ge indicate that the methods used here can produce mostly single high-resistivity crystals of significant size. The results in other cases show that there are still variables to be identified and brought under control.

SECTION 3

MEASUREMENTS AND EXPERIMENTS WITH Si-Ge CRYSTALS

A. COMPOSITION

Table 2 shows the distribution of Ge between the melt and the crystal for seven growth runs. The crystal composition was determined by electron microprobe analysis on the tang end over the entire area. The 2σ limits are listed to show the excellent radial uniformity. The composition is also uniform in the axial direction because only a small fraction of the melt is crystallized. The only exception is C087, which weighs about 50 g (corresponding to 17% of the melt). By calculation, the Ge concentration increases by approximately 12% from the seed to the tang end.

The effective distribution coefficient, which is about equal to the equilibrium value because of the slow growth rate, varies from 0.37 to 0.40 for crystals of approximately 10% Ge content. This is in fairly good agreement with the value calculated from the reported equilibrium phase diagram.

Table 2. Composition of Si-Ge Crystals

Crystal	Melt Composition		Crystal Composition		Ge 2σ Limits	Number of Analyses	Effective Distribution Coefficient
	Si	Ge	Si	Ge			
C056	0.902	0.098	0.967	0.033	—	1	0.34
C059	0.84	0.16	0.93	0.069	—	1	0.43
C065	0.64	0.36	0.864	0.136	0.0008	4	0.38
C068	0.72	0.28	0.909	0.091	0.0012	4	0.39
C074	0.72	0.28	0.8923	0.1077	0.0012	7	0.38
C077	0.72	0.28	0.8885	0.1115	0.0016	6	0.40
C087	0.72	0.28	0.8836	0.116	—	5	0.37 ^a

^aCalculated assuming 12% increase in the Ge content from seed to tang end.

6397

A wafer from crystal C064 was polished and scanned over a distance of 90 μm by the electron microprobe to determine whether there were microscopic variations in composition. The volume probed in this scan was about 1 μm^3 . Figure 2 shows the actual scan, which indicates that the composition is uniform within the measurement noise, corresponding to approximately 2.5% of the Si concentration. Thus, at least within the accuracy of measurement, there is no clustering or segregation effect in our material, in contrast to behavior that had been reported for 50% Si-Ge alloys.

B. IMPURITIES IN Si-Ge

1. Oxygen

Oxygen is a natural contaminant in Si-Ge grown from an SiO_2 crucible at high temperatures. Its concentration in crystal C077 was determined by measuring the room-temperature infrared absorption at 9 μm .

C077 as grown was n-type and had a resistivity between 2000 and 6000 $\Omega\text{-cm}$ at ambient temperature. After 1 hr annealing at 650°C to decompose the oxygen donor complex, it changed to p-type with approximately 1700 $\Omega\text{-cm}$ resistivity. Because of the unexpectedly large concentration of oxygen indicated by this result, we decided to measure it by way of the IR absorption.

The as-grown crystal was sliced to a thickness of 0.072 in. and then polished on both sides. A Beckman IR12 spectrometer was used to measure the absorption. The absorption coefficient at 9 μm was 1.39 cm^{-1} . This corresponded to $3.8 \times 10^{17} \text{ cm}^{-3}$ according to the calibration curve by Kaiser and Keck¹ for oxygen in Si. Assuming a growth temperature of 1340°C for the 30% Ge melt, the value is below the solubility of oxygen in Si determined by Logan and Peters.²

¹Kaiser and Keck (JAP 28, 822, (1957)).

²Logan and Peters (JAP 30, 1827 (1959)).

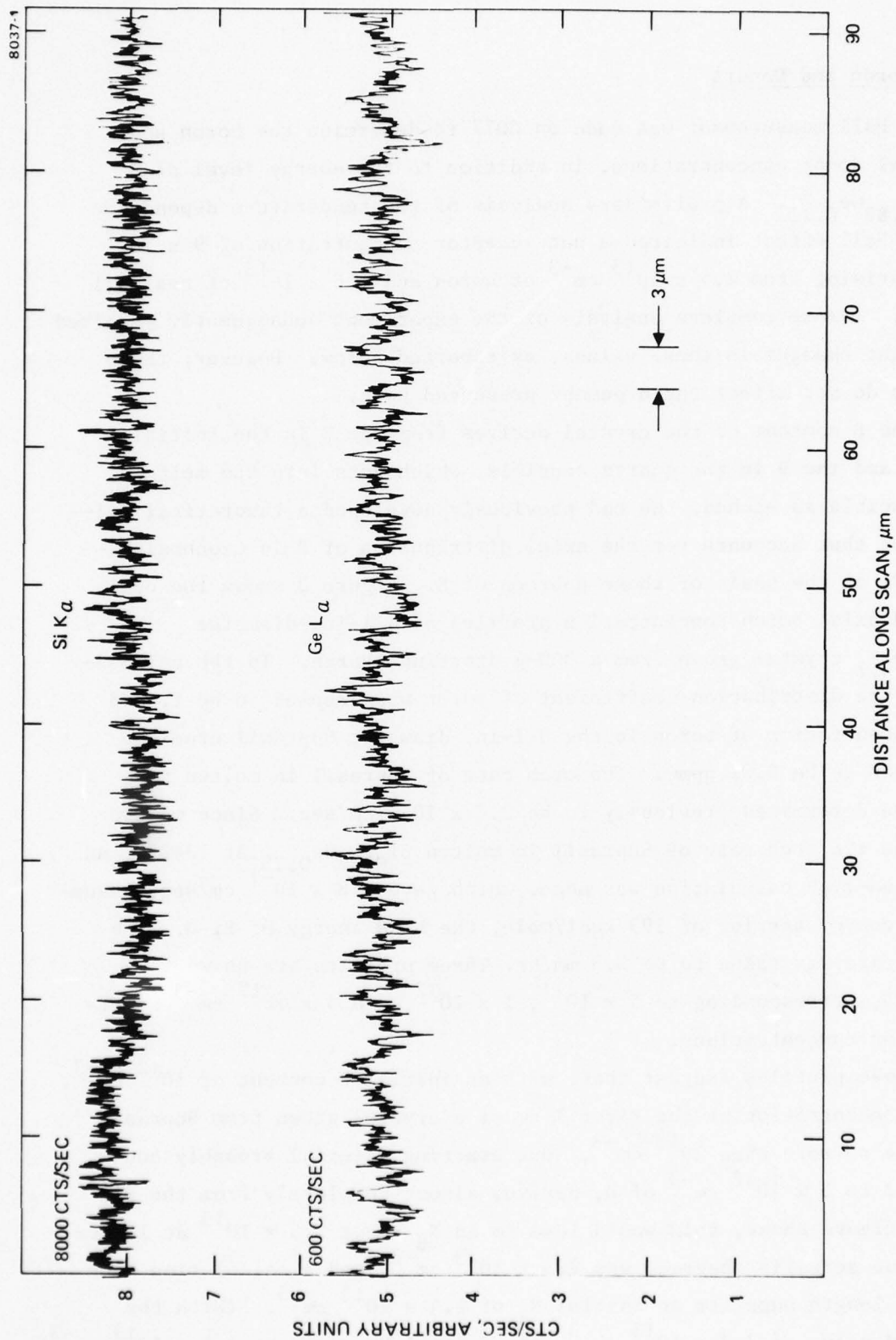


Figure 2. Electron microprobe scan of C064 Ge. The ordinate is in arbitrary units, equal to about 100 for Ge and 1000 for Si.

2. Boron and Donors

A Hall measurement was made on C077 to determine the boron and residual donor concentrations, in addition to the energy level of B in $\text{Si}_{0.89}\text{Ge}_{0.11}$. A preliminary analysis of the temperature dependence of the Hall effect indicated a net acceptor concentration of $9 \times 10^{12} \text{ cm}^{-3}$, arising from $2.5 \times 10^{13} \text{ cm}^{-3}$ of boron and 1.6×10^{13} of residual donors. A more complete analysis of the experiment subsequently resulted in slight changes in these values, as reported below. However, these changes do not affect the argument presented here.

The B content of the crystal derives from the B in the initial charge and the B in the quartz crucible, which gets into the melt as the crucible is etched. We had previously developed a theoretical calculation that accounts for the axial distribution of B in Czochralski-grown Si on the basis of these sources of B. Figure 3 shows the calculated axial boron concentration profiles of a 1-in.-diameter $\text{Si}_{0.9}\text{Ge}_{0.1}$ crystal grown from a 300-g starting charge. In the calculations, the distribution coefficient of boron was assumed to be 1, and the concentration of boron in the 3.1-in.-diameter Suprasil crucible was taken to be 0.01 ppmw. The etch rate of Suprasil in molten Si had been determined previously to be $2.2 \times 10^{-6} \text{ cm/sec}$. Since we did not have the etch rate of Suprasil in molten $\text{Si}_{0.72}\text{Ge}_{0.28}$ at 1340°C , an Arrhenius-type calculation was made, which gave $1.8 \times 10^{-7} \text{ cm/sec}$, assuming an energy barrier of 193 kcal/mole, the bond energy of Si-O. The growth rate was taken to be 0.5 mm/hr. Three profiles are shown in Figure 3, corresponding to 5×10^{11} , 1×10^{12} , and $5 \times 10^{12} \text{ cm}^{-3}$ starting boron concentrations.

These profiles suggest that, with an initial B content of 10^{12} cm^{-3} , the B concentration of the first 1 cm of a crystal grown from Suprasil would be no more than 10^{13} cm^{-3} . Our starting material probably contained 2 to $3 \times 10^{12} \text{ cm}^{-3}$ of B, derived almost completely from the Si. As the figure shows, this would lead to an N_B about 1.5×10^{13} at 1.6 cm. The value actually observed was $2.5 \times 10^{13} \text{ cm}^{-3}$, and a calculation back to zero length suggests an initial N_B of $1.4 \times 10^{13} \text{ cm}^{-3}$. (With the modified value of $2.2 \times 10^{13} \text{ cm}^{-3}$, the initial N_B would be $1.1 \times 10^{13} \text{ cm}^{-3}$).

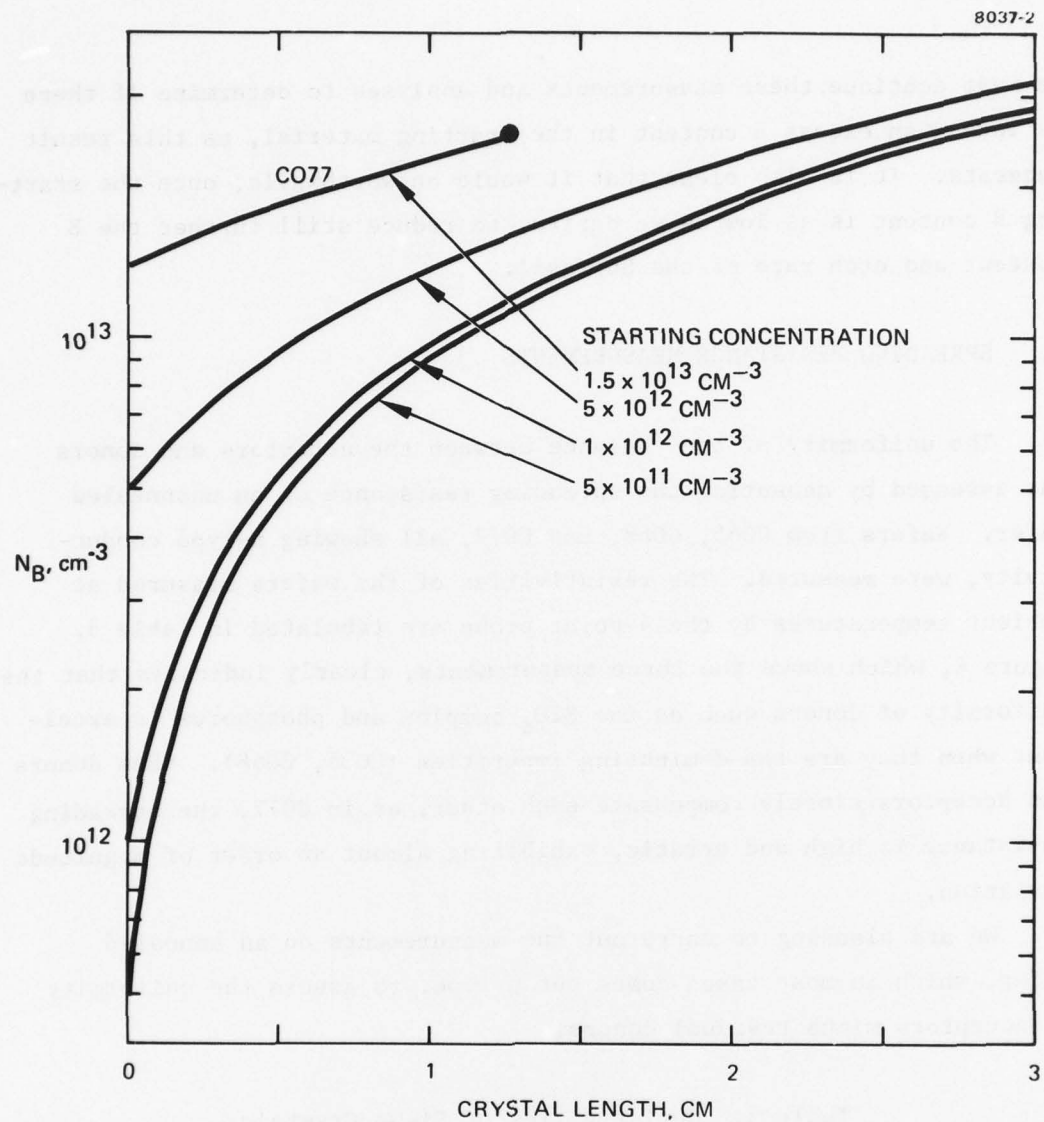


Figure 3. Axial boron concentration of 1-in.-diameter crystal of $\text{Si}_{0.9}\text{Ge}_{0.1}$ initial composition, and crystal CO77 (1.3 in. diameter).

We must continue these measurements and analyses to determine if there is indeed an excess B content in the starting material, as this result suggests. It is also clear that it would be worthwhile, once the starting B content is as low as we desire, to reduce still further the B content and etch rate of the Suprasil.

C. SPREADING RESISTANCE MEASUREMENTS

The uniformity of the balance between the acceptors and donors was assessed by measuring the spreading resistance on an unannealed wafer. Wafers from C065, C068, and C077, all showing n-type conductivity, were measured. The resistivities of the wafers measured at ambient temperatures by the 4-point probe are tabulated in Table 3. Figure 4, which shows the three measurements, clearly indicates that the uniformity of donors such as the SiO_4 complex and phosphorus is excellent when they are the dominating impurities (C065, C068). When donors and acceptors closely compensate each other, as in C077, the spreading resistance is high and erratic, exhibiting almost an order of magnitude variation.

We are planning to carry out the measurements on an annealed wafer, which in most cases comes out p type, to assess the uniformity of acceptors minus residual donors.

Table 3. Resistivities of Si-Ge Crystals

Crystal Number	Resistivity, $\Omega\text{-cm}$
C065	760
C068	690
C077	2,000 - 6,000

6397

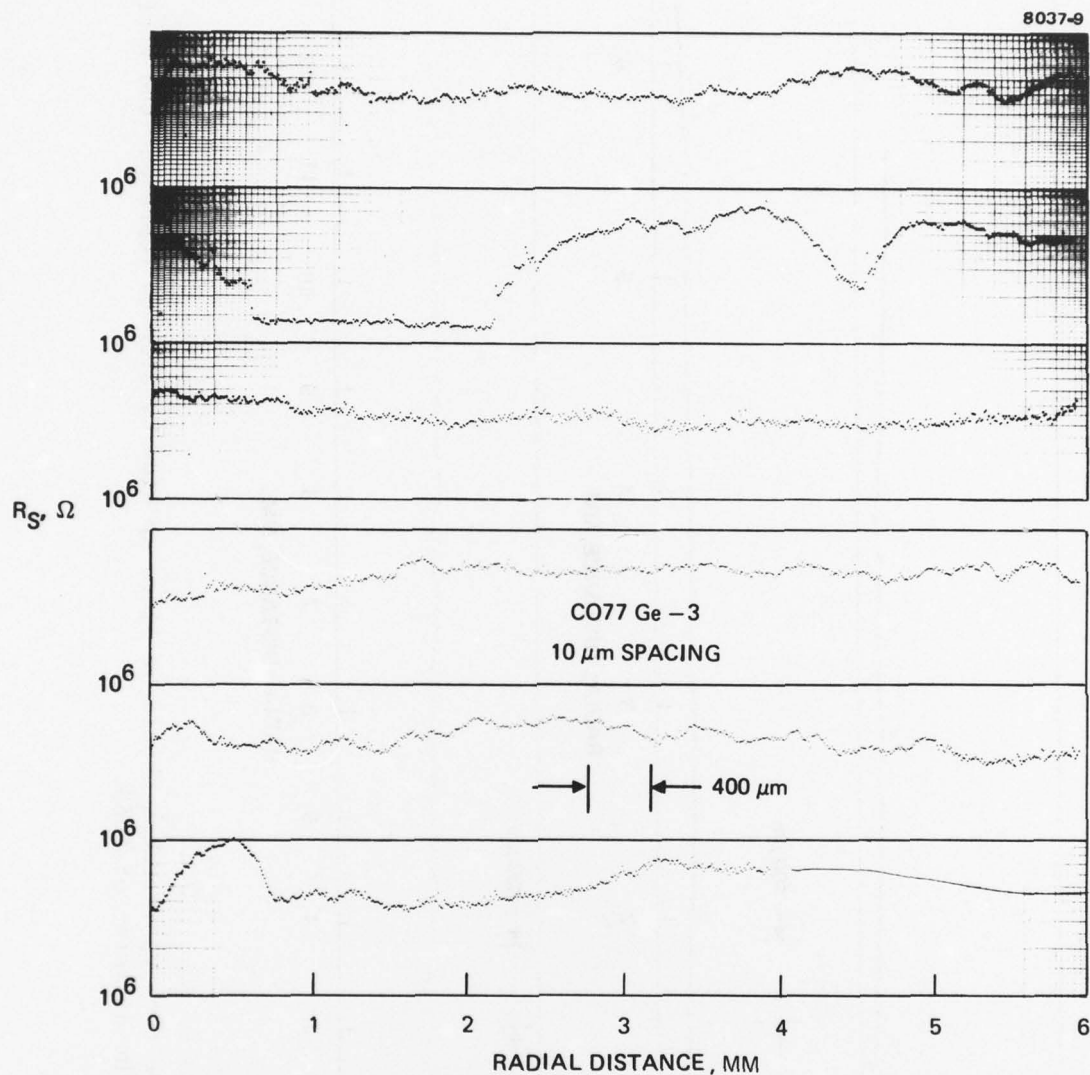


Figure 4. Spreading resistance of Si-Ge crystals. The six traces should be lined up side by side; each one represents 6 mm of a trace across the 36 mm diameter of the wafer.

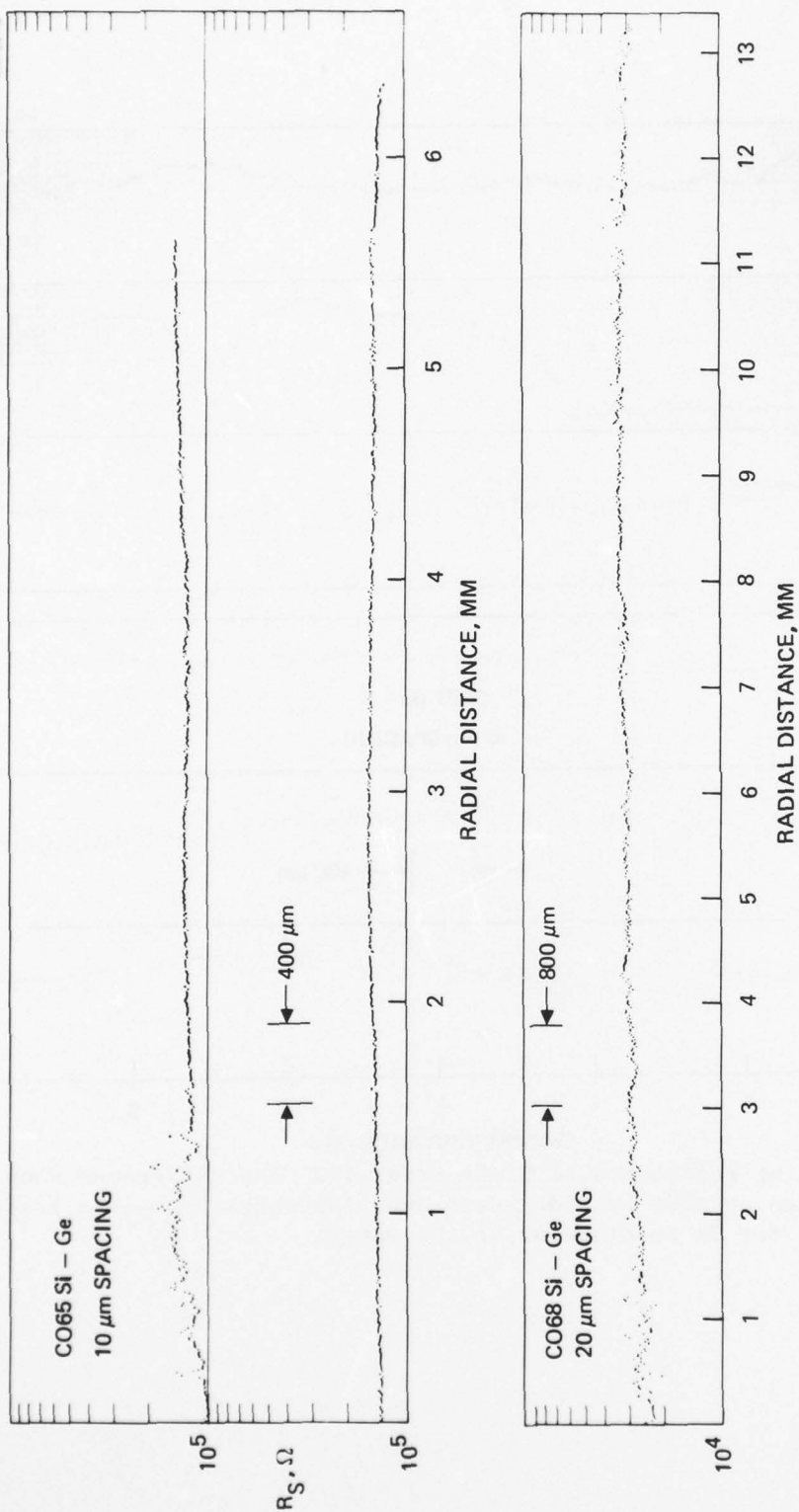


Figure 4. Continued. The two upper traces should be lined up side by side to represent the variation of R_S across the diameter of C065.

D. OPTICAL ABSORPTION COEFFICIENT AT 1.06 μm

The absorption coefficients at 1.06 μm were initially determined on crystals C065 ($\text{Si}_{86.43}\text{Ge}_{13.57}$) and C068 ($\text{Si}_{90.95}\text{Ge}_{9.05}$). The absorption coefficients were 68 cm^{-1} and 54 cm^{-1} for C065 and C068, respectively.

Figure 5 shows the absorption curve of crystal C077 ($\text{Si}_{88.85}\text{Ge}_{11.15}$). The absorption coefficient at 1.06 μm was 51 cm^{-1} , which was not consistent with the values from C065 and C068. We are continuing our investigation to obtain a more definite correlation with the alloy composition.

E. ANALYSIS OF HALL MEASUREMENTS

The carrier concentration, p , versus temperature, shown in Figure 6, fits reasonably well to the model of a single, compensated acceptor level with an ionization energy of 0.0427 ± 0.0002 eV. This energy is significantly less than the ionization energy of 0.0457 ± 0.0003 eV for B in pure Si.³ The apparent increase in p at temperatures above 150 K is an artifact of assuming the scattering factor of $r \equiv 1$ in calculating p from

$$p = \frac{r}{eR_H},$$

where R_H is the Hall coefficient. This apparent increase in p reflects the fact that r has a large temperature dependence in this temperature range.⁴ Analysis of the data was restricted to $T \leq 66.7$ K to avoid this effect. In least-squares fitting the charge balance equation

³A. Baldereschi and N.O. Lipari, Proc. of 13th International Conf. on the Physics of Semiconductors, Edited F.G. Fumi (Typografia Marves, Rome, 1976) p. 595.

⁴R. Baron, M.H. Young, J.K. Neeland, and O.J. Marsh, Proc. of the 3rd International Symposium on Silicon Materials Science and Technology, Edited by H.R. Hugg and E. Sirtl (The Electrochemical Society, 1977) p. 367.

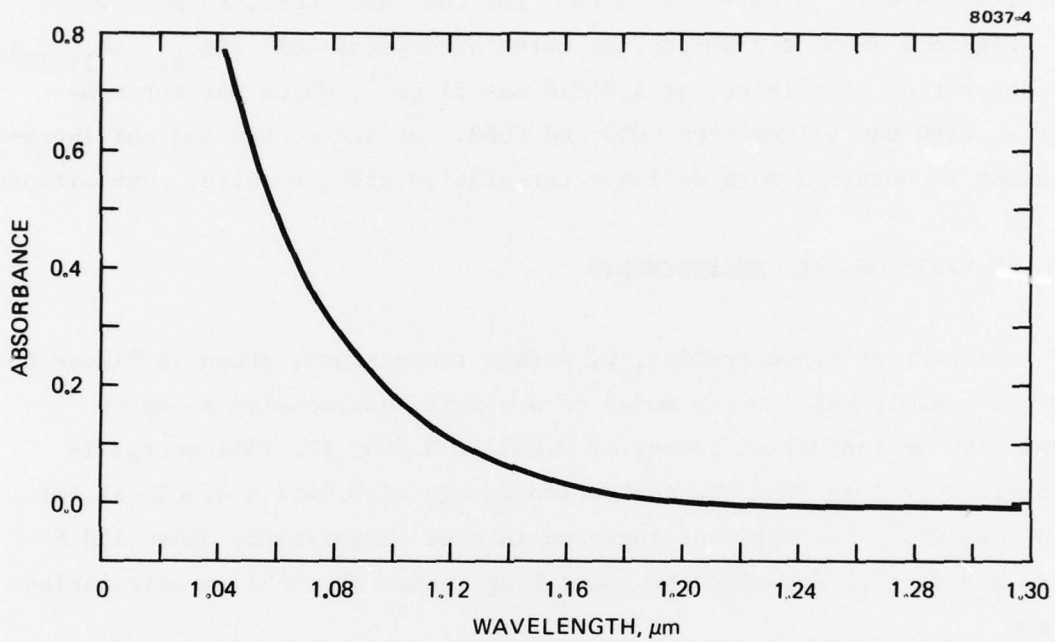


Figure 5. Absorption spectrum of C077 Ge at 296°K. Sample thickness: 0.009 in.

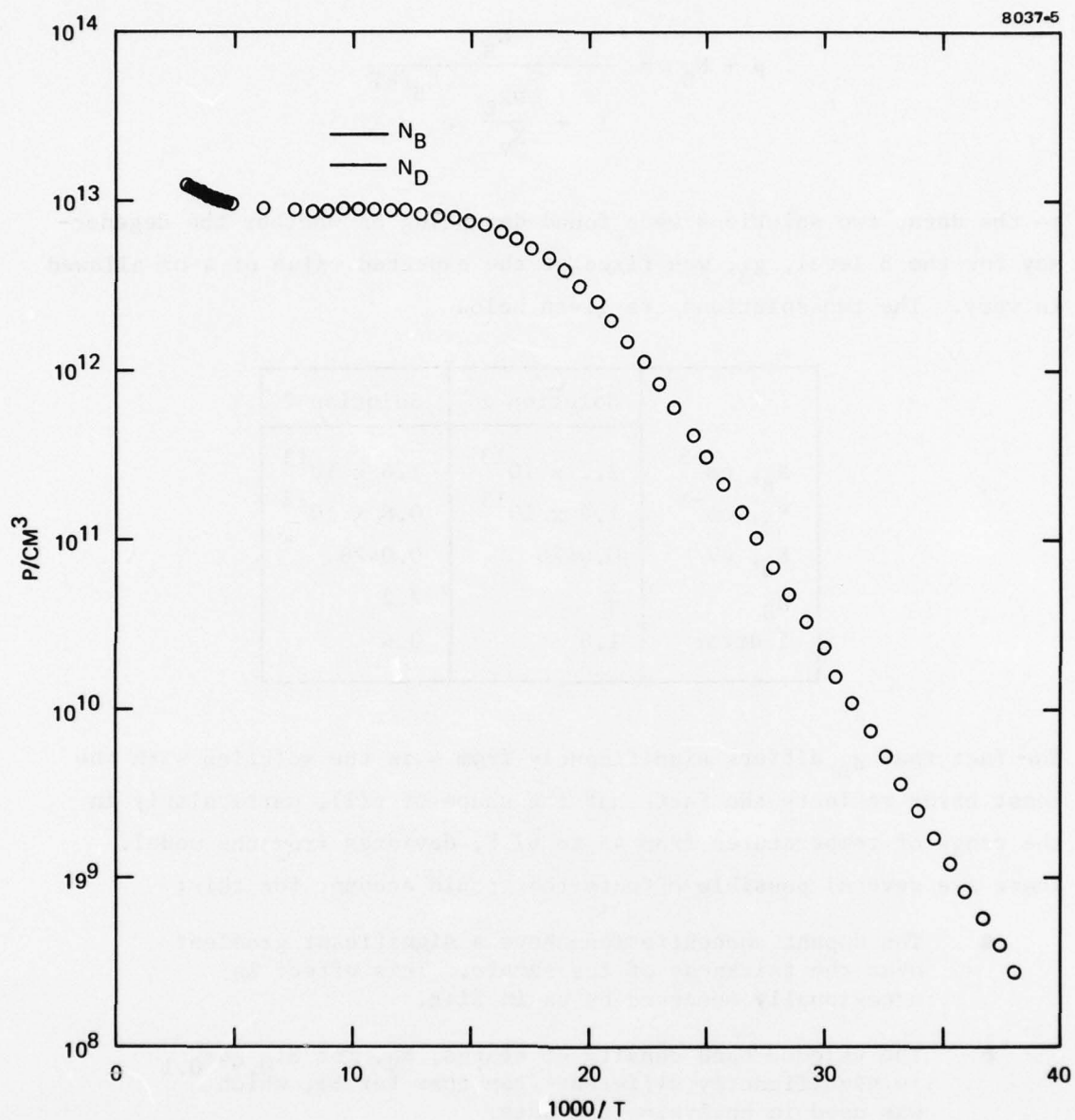


Figure 6. Carrier concentration vs reciprocal temperature Si-Ge alloy C077Ge.

$$p + N_D = \frac{N_B}{1 + \frac{pg_B}{N_V} e^{E_B/kT}}$$

to the data, two solutions were found depending on whether the degeneracy for the B level, g_B , was fixed at the expected value of 4 or allowed to vary. The two solutions are given below

	Solution 1	Solution 2
$N_B, \text{ cm}^{-3}$	2.2×10^{13}	1.6×10^{13}
$N_D, \text{ cm}^{-3}$	1.4×10^{13}	0.8×10^{13}
$E_B, \text{ eV}$	0.0426	0.0428
g_B	4	7.2
% error	1.8	0.4

The fact that g_B differs significantly from 4 in the solution with the least error reflects the fact that the shape of $p(T)$, particularly in the range of temperatures from 45 to 67 K, deviates from the model. There are several possible effects that could account for this:

- The dopant concentrations have a significant gradient over the thickness of the sample. This effect is occasionally observed by us in Si:B.
- The valence band density of states, N_V , for $\text{Si}_{0.9}\text{Ge}_{0.1}$ is significantly different from that for Si, which was used in analyzing the data.
- The ionization energy of boron in $\text{Si}_{0.9}\text{Ge}_{0.1}$ is not a single value: rather, it is a distribution of values corresponding to the distribution of nearest-neighbor environments of the B atoms.

The latter effect is probably the one responsible, as a similar effect was observed for In in its photoconductive spectrum. Until a model for the distribution of E_B is developed, it will not be clear which of the solutions given above is the better one.

The mobility, shown in Figure 7, is as expected and shows the influence of alloy scattering.

The relatively high donor concentration found could be residual donor activity from Si-O complexes. The sample was annealed at 650°C for 1 hr to remove donor activity caused by these complexes, which form at temperatures of about 450°C and are normally present in an as-grown Cz crystal. This anneal is normally sufficient to eliminate this activity in Si, but it is possible that Si:Ge may require a different anneal to accomplish this.

F. X-RAY TOPOGRAPHS

To establish the degree of crystal perfection, survey-type X-ray diffraction topographs were made of Si:Ge alloys in the range from about 5 to 15 at.% Ge. All of the crystals examined exhibited some structure in the topographs; examples are shown in Figure 8. The following major crystal defects were noted:

- Twin lamellae, sometimes resulting in hexagrams about the $\langle 111 \rangle$ growth axis
- "Tree ring" contrast contours about the growth axis
- Globular areas of no contrast.

The twinning system $\{111\} \langle 112 \rangle$ results in $\langle 115 \rangle$ of the twin lying along the same direction as $\langle 111 \rangle$ of the untwinned crystal. Six permutations of this twin system are possible along the $\langle 111 \rangle$ growth axes, generating the hexagram visible in some of the topographs.

Local variation in lattice parameters gives rise to the "tree ring" contrast seen in the topographs. This structure can be attributed to compositional variation in the alloy and/or to segregation of a foreign species.

Whenever there is a polycrystalline inclusion or a grossly mis-oriented region in a crystal, the result on the X-ray topograph will be an area of no contrast.

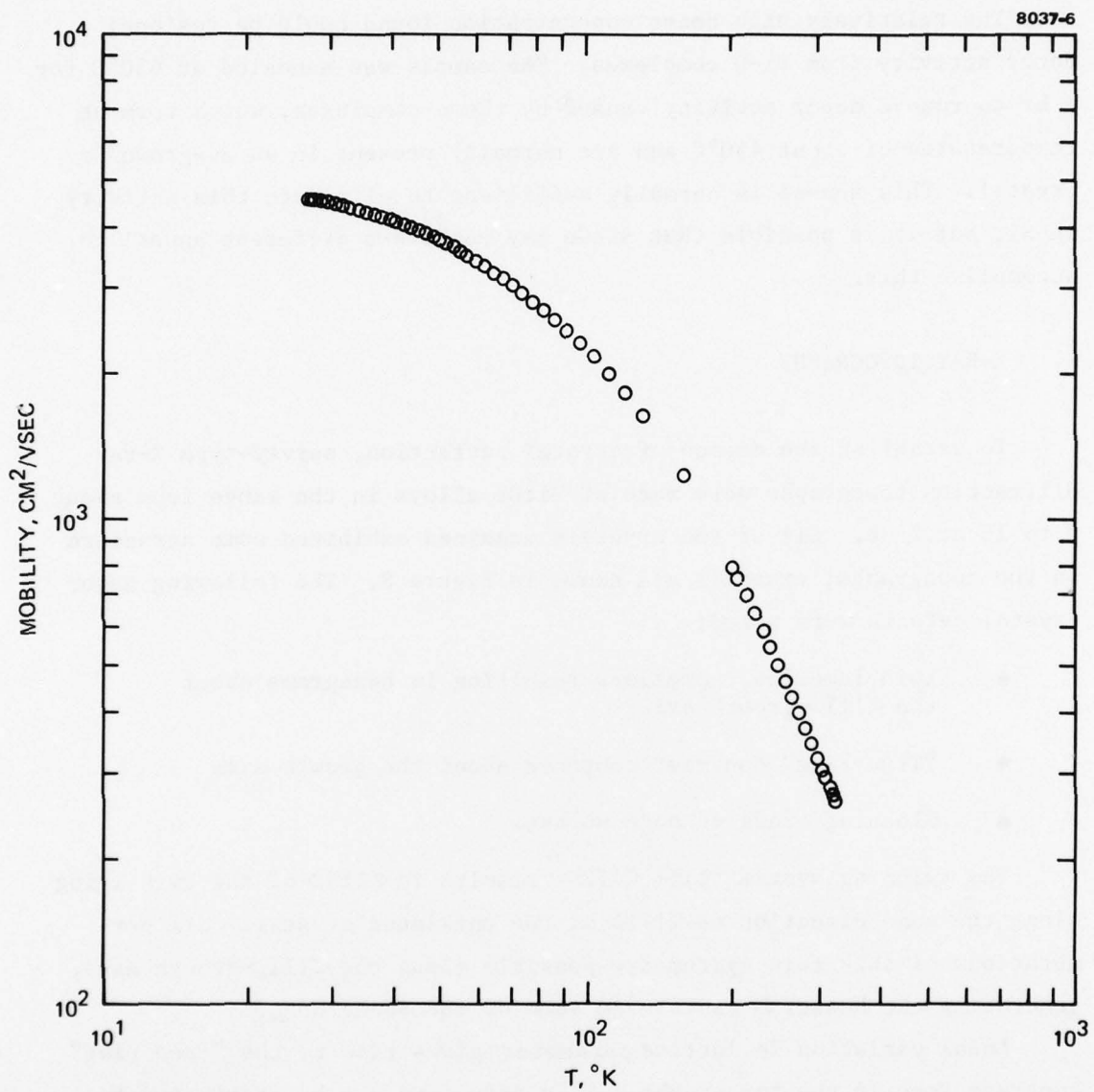
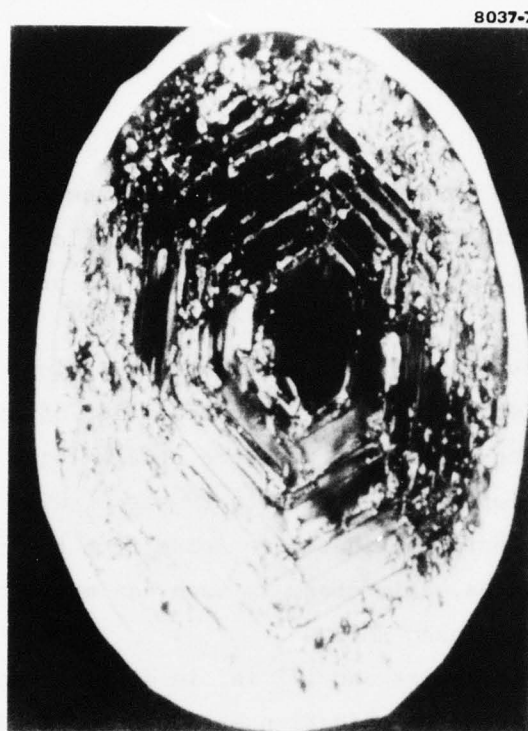
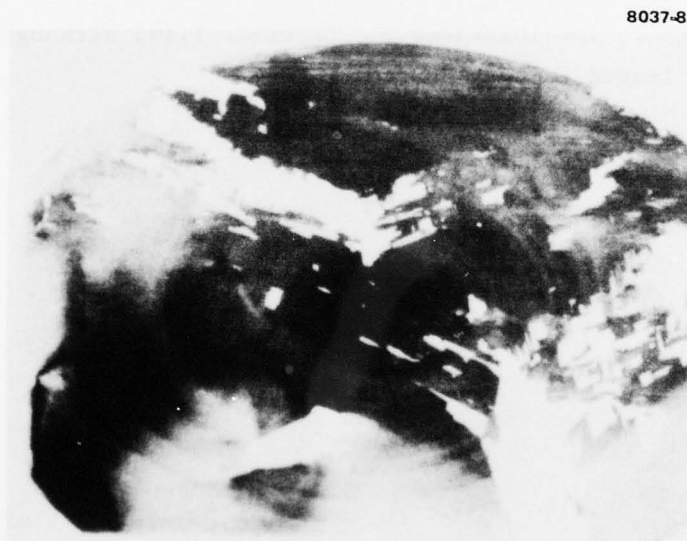


Figure 7. Mobility versus temperature Si-Ge alloy C077Ge.



(a) CO21



(b) CO64

Figure 8. X-ray topographs. CO21 was grown before the beginning of the program.

G. OXIDATION OF Si-Ge

We have begun to investigate some of the processing steps that will be necessary to fabricate detectors from Si-Ge alloys. It will surely be necessary to modify, or at least to check, the procedures used with Si.

A procedure developed for the enhanced oxidation of Si at low temperature was tried on C065, with a composition of $\text{Si}_{0.864}\text{Ge}_{0.136}$. In the thermal oxidation of Si, the presence of a halogen enhances oxidation. We have developed a procedure that uses O_2 with chloroform as the halogen source for thermal oxidation. Aside from the smooth and uniform oxide layer it produces, chloroform is much easier to handle and transport than the commonly used HCl.

A wafer 0.018 in. thick and 1/2 in. in diameter was polished on both sides and subjected to oxidation at 900°C for 4 hr. The chloroform was transported at ambient temperature into the chamber using He as a carrier gas. The thickness of the oxide film, although not measured, was estimated to be $\sim 1500 \text{ \AA}$.

SECTION 4

PRESENT STATUS AND FUTURE PLANS

It is a major achievement to have produced high-resistivity largely single Si-Ge up to 13% Ge. The keys to this success were in using a 1-in. shoulder as a seed and high-purity synthetic quartz (Suprasil) crucibles. With an ordinary small-diameter seed and the necessary slow growth rate, many hours would have been required to grow the seed out to a 1-in. diameter; during that period the growing crystal would have been susceptible to twinning, loss of crystallinity, and contamination. It was unexpected that we could go from a shoulder containing 0.5% Ge to an alloy of 13% Ge in one step.

The relatively high resistivity we obtained is associated with the use of high-purity synthetic quartz crucibles, which help eliminate contamination from the etching of the crucible by the melt and preserve the purity of the starting charge. We hope that it will be possible to attain resistivities high enough for PIN detectors by this method; we plan to use Hall-effect measurements to identify the residual impurities and to schedule further growth runs to eliminate these impurities.

Since our results suggest that the major source of boron in our Si-Ge crystals is either the etching by the melt of the quartz crucible or the handling, we will concentrate on these issues. We will institute higher standards of purity in preparing the charge and the crucible, and we will grow a series of short crystals (a few millimeters at most) to examine the effect of a shorter exposure of the crucible to the melt. A possible outcome is that short crystals, grown from a melt that has been in contact with the crucible for only a relatively short time, will have a lower boron (and phosphorus) content than longer crystals requiring a 20 or 30 hr growth time. This procedure may be sufficient to provide high-resistivity material suitable for intrinsic detector studies. If the resistivity obtained is not high enough, we will adopt the alternative, the pedestal growth method. Even before completing the growth

runs aimed at high resistivity, we will schedule the growth of indium-doped Si-Ge alloy at several different Ge and In contents. The concentrations of boron in our undoped crystals compare very favorably with those in useful indium-doped silicon, and we expect that the Czochralski growth procedure already developed for undoped alloys can be extended to provide material for extrinsic detector evaluation.

We expect that by 15 February 1979 we will have produced Si-Ge suitable for PIN detectors either by the Czochralski technique or by a pedestal (crucible-free) method. By the same time, Si-Ge:In will have been grown and evaluated as a potential monolithic detector array substrate for 8 to 14 μm . We expect to discuss these results with AFML and reach a decision as to the distribution of emphasis during the rest of the technical effort. Although the present program plan calls for the fabrication of 1.06 μm detectors by using an existing Si process for Si-Ge, it will probably be necessary to modify the process steps to make a fair test of Si-Ge's promise. Therefore, we recommend devoting some of the program effort to an investigation of elementary process step modifications required to adapt silicon device fabrication procedures to silicon-germanium.